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(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors: GLASS, J., Edward ; 1751 South 23rd Street, Fargo, ND 58103 (US). LUNDBERG, David, John ; 2368 Mailand Court, Maplewood, MN 55119 (US).

(74) Agents: GOULD, David, J. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

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(54) Title: DISPERSANT TREATED PIGMENTS

(57) Abstract

A pigment particle, in particular TiO_2, having absorbed on its surface a hydrophobically modified dispersant interacting with a hydrophobe-modified water-soluble polymer associate thickener is disclosed which when used as a component of a latex paint formulation results in dried films with improved gloss properties.

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DISPERSANT TREATED PIGMENTS

BACKGROUND OF THE INVENTION

1-Field of the Invention

The invention relates to dispersant treated pigment for use in aqueous paint formulations which result in dried films with improved gloss properties.

2-Description of the Prior Art

An aqueous paint formulation represents a union of separate disperse systems including suspensions of polymer colloid (latex) and pigment. Film formation occurs by fusion of the latex (binder) particles after the water evaporates. Film gloss largely depends on paint viscosity. Pigment contributes to gloss in a negative way. Pigment aggregates that penetrate the smooth paint surface cause random light scattering, thus decreasing specular reflection or gloss. Thus, the use of dispersants to enhance pigment dispersion is important. Thickeners are used in emulsion paints to increase viscosity at high shear rates by increasing the applied film thickness and hence improving flow and leveling. Appropriate viscosity at high shear is needed to provide correct brush drag for proper spreading rate and coverage uniformity. Associate thickeners are used for this purpose and, in general, are hydrophobically-modified water-soluble polymers.

The influence of associated thickeners on coating performance has been extensively described by J.E. Glass et al.; e.g. (I) J. Oil, Color Chemists Assn. (1984), 67(10), 256; (II) ibid (1984), 67 (11), 279; (III) ibid (1986), 69(10), 263; (IV) ibid (1988), 71(10), 315; (V) Prog. Org. Coatings (1989), 17, 155- 173.

U.S. Patent 4,177,081 discloses an aqueous slurry of TiO_2 pigment to provide a high gloss finish to paint films derived from acrylic water based systems. It describes the use of a suitable pigment dispersant system.

U.S. Patent 4,110,292 discloses a method of producing a high gloss, air drying water base, pigmented latex paint by grinding a pigment into a water-free solution of a carboxyl-functional addition solution copolymerized copolymer of a monoethylenically unsaturated monomers including at least about 10% by weight of a monoethylenically unsaturated carboxylic acid in water miscible alcoholic organic solvent, the copolymer being at least partially neutralized at the time of grinding with an hydroxy amine, to render the copolymer dispersible in water, and thereby form a nonaqueous pigment paste, and then mixing the nonaqueous pigment paste with an air drying aqueous latex dispersion obtained with an aqueous emulsion copolymerization.

U.S. Patent 4,735,981 discloses combinations of associative thickeners and aqueous latex paints. Alkaline aqueous latex paints are disclosed which contain a combination of thickeners constituted by: (I) a urethane polymer having at least three hydrophobic groups, at least two of which are terminal hydrophobic groups linked by hydrophilic groups; and (II) an alkali soluble aqueous emulsion copolymer of; (A) about 20-70 weight percent of an alpha, beta monoethylenically unsaturated carboxylic acid, typically methacrylic acid; (B) about 20-80 weight percent of a monoethylenically unsaturated monomer lacking surfactant capacity, typically ethyl acrylate; (C) about 0.5-60 weight percent of a nonionic urethane monomer which is the urethane reaction product of a monohydric nonionic surfactant with a monoethylenically unsaturated monoisocyanate; and (D) from 0 up to about 2 weight percent of a polyethylenically unsaturated monomer.

U.S. Patent 4,722,962 discloses nonionic associative thickeners, suitable for use in aqueous coating compositions, comprising a water soluble polymer of (a) from about 40 percent to about 98 percent, preferably from 60-95 percent by weight of a monoethylenically unsaturated monomer such as acrylamide, N,N-dimethyl acrylamide, vinyl pyrrolidone, hydroxyethyl acrylate and mixtures thereof; and (b) from about 2 percent to about 60 percent, preferably from 5 to 40 percent, by weight of a nonionic urethane monomer which is the reaction product of a monohydric nonionic surfactant with a monoethylenically unsaturated monoisocyanate. The monohydric nonionic surfactants suitable for use in component (b) include ethoxylated hydrophobes containing adducted ethylene oxide to provide the hydrophilic portion of the molecule. The hydrophobes usually include an aliphatic alcohol or alkyl phenol in which a carbon chain containing at least 6 carbon atoms provides the hydrophobic portion of the surfactant. These surfactants are illustrated by ethylene oxide adducts of dodecyl, octyl alcohol, nonyl phenol and dinoyl phenol which are commercially available and which contain from about 5 to 150 moles, preferably from 10 to 60 moles of ethylene oxide per mole of hydrophobe.

U.S. Patent 4,079,028 discloses latex and other aqueous systems thickened by low molecular weight urethane polymers having at least three hydrophobic groups interconnected by hydrophilic polyether groups. It is mentioned in column 7, lines 54-56, that in latex paints, polymers of the invention can provide excellent flow and leveling as well as thickening.

U.S. Patent 4,426,486 discloses water-soluble thermoplastic organic polymers, having segments of bunched monovalent hydrophobic groups, which provide improved thickening and leveling in aqueous systems. The polymers have a weight average molecular weight of at least about 10,000.

SUMMARY OF THE INVENTION

This invention relates to pigment particles having absorbed on their surface an hydrophobically modified dispersant interacting with an associate thickener which is a hydrophobe modified water soluble polymer. The pigment particle when used in a paint provides improved thickening efficiency and produces a dried paint film of superior gloss.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Pigment

Any pigment used in the paint industry can be used in the present invention. The preferred pigment is TiO_2 of a type used in latex paints.

The TiO_2 particles, if desired, may be pretreated with various inorganic surface treatments, including silica and alumina. Numerous TiO_2 pigments are available from commercial sources, such as E.I. DuPont de Nemours and Co. products TiPure R-900, R-902 and R-960.

The TiO_2 particles will preferably be of uniformly small particle size with at least 95 mass percent of the average particle size being one micron or less and with an average particle size of less than about 0.6 microns.

The pigment volume concentration in the paint can range in the known fashion. A pigment volume concentration of at least 10% is usual, at least 20% is preferred. The examples use 21% pigment volume concentration.

Dispersants

Dispersants of the invention have a proton donating component to achieve adsorption on the pigment surface and a hydrophobic portion to facilitate adsorption on the pigment surface and to provide sites for hydrophobic interaction with the associate thickeners.

Hydrophobic acid copolymers such as the co-oligomer of maleic acid and alpha olefins have been found to provide sufficient hydrophobic sites and to be highly absorbed on the surface of the pigment in alkaline media. This is believed to be due in part to the difference in pK_a of 1,2 contigious carboxyl units, relative to 1,3 alternating acid groups and in part to the presence of the repeating hydrophobic group. There are believed to be interactions between neighboring hydrophobic and carboxyl groups that lower the dielectric constant in the area around the carboxyls contigious to the hydrophobic groups.

The olefins of preference are alpha olefins having 5 to 25 carbon atoms, either branched or straight chained. More preferred are olefins having 10-18 carbon atoms.

Examples of suitable alpha olefins include diisobutylene, a branched olefin with 8 carbons and 5 carbons in the main chain, 1 - decene, a straight chain olefin with 10 carbon atoms, 1 - tetradecene, a straight chain olefin with 14 carbon atoms, and 1 - octadecene, a straight chain olefin with 18 carbon atoms. These olefins are hydrophobic and substantially alternate with the maleic acid in the copolymer.

Appropriate dispersants of this invention are illustrated by

(I) TAMOL 731, a diisobutylene-maleic acid copolymer hydrophobic dispersant sold by Rohm and Haas Co.; and

(II) alpha-olefin/maleic acid copolymers with alpha-olefin groups such as 1-decene (AO[C10]/MA), 1-tetradecene (AO[C14]/MA, and 1-octadecene (AO[C18]/MA).

The concentration of the dispersant, most often expressed as a weight percent based on the pigment, can effect the paint in negative manner if formulated at too high or low a level. The optimum dispersant levels is found by making slurries of varying dispersant levels and finding the level at which the viscosity is at a desired minimum. The formulation level is then increased, usually about 30% above the concentration at the viscosity minimum, to assure a level high enough to keep the pigment from flocculating. The average level is usually from 0.3 to 1.5 grams dispersant per 100 grams of pigment when TiO_2 is the pigment. Most preferred is about 0.75 gram dispersant per 100 grams of pigment.

Associate Thickeners

The thickeners useful in the present invention contain hydrophobes which can interact with the dispersant absorbed on the pigment particle. It is believed that this interaction provides steric stabilization to the electrostatic forces provided by the dispersant's absorption and provides a greater barrier to flocculation of the pigment and thereby improvement in the film gloss.

The amount of thickener which interacts with the dispersant treated pigment particle is proportional to the amount of dispersant absorbed on the pigment surface, and to the size of the hydrophobic portion of the dispersant.

Associate thickeners of the invention include

(I) hydrophobe modified ethoxylated-urethane polymers (HEUR), preferable, wherein the hydrophobe is low molecular weight.

Suitable HEUR products are available from commercial sources such as, Rohm and Haas, under the product designations, RM-825, QR-708, RM-708, RM-825 and RM-1020; and Union Carbide, under the product designations, SCT-200, SCT-215, SCT-270, and SCT-275;

(II) polymers formed by reacting various diisocyanates with a hydrophobe-containing poly(ethyleneoxide)$_x$ wherein x is 1-250 preferably about 25 to 100. The diioscyanate may alipathic, cycloalipathic, or aromatic, but preferably is an olefinic diisocyanate. Preferably there is one mole of hydrophobe per every 10-100 moles, more preferably about per every 100 moles, of ethylene oxide.

Useful hydrophobe groups contained 4 to 18 carbon atoms, such as, cyclohexyl, octyl, octadecyl, dodecyl, octyl phenyl and nonyl phenyl.

(III) polymers formed by reacting poly(oxyethylene)$_y$, wherein y is 50 to 750, preferably 300 to 650, sequentially with a suitable diisocyanate, such as, isophorone diisocyanate, and then with a C4-C4-C18 alcohol or C7-C18 alkylphenol.

The hydrophobe portion of the alcohol or alkylphenyl contain C4-C18 carbon atoms, such as, cyclohexyl, octyl, octadecyl, dodecyl, octyl phenyl and nonyl phenyl.

Specific associated thickeners of these types (II) and (III) include the following:

(A) reaction products of a biuret of hexamethylene diisocyanate and a nonyl phenol surfactant containing from 50-100 ethylene oxide units, e.g., 50 or 100 units as in (NP50C6)3N, and (NP100C6)3N;

(B) reaction products of tetramethylxylene diisocyanate with a nonyl phenol surfactant containing 100 ethylene oxide units, e.g., (NP100)2TMXDI;

(C) reaction products of octyl phenol with the isocyanate groups formed by reacting polyethylene glycol of about 595 repeating units with isophorone diisocyanate, e.g., C8IP(EtO)595IP8.

The amount of associated thickener added to the paint formulation is the amount sufficient to obtain the desired stormer visocity (KU) of 80-100. Normally the amount ranges from .20 to 2.50 grams per 100 grams of water.

Latex

Any conventional air drying emulsion latex used in the paint industry may be employed with the invention herein, such as, acrylic and vinyl acetate polymers. "Acrylic polymer" means any polymer wherein at least 50% by weight is an acrylic or methacrylic acid or ester, including mixtures of such acids and esters individually and together. The term "vinyl acetate polymer" means any polymer containing at least 50% by weight of vinyl acetate. The more usual polymers include vinyl acetate-butyl acrylate copolymers, vinyl acetate-ethylene

copolymers, and methyl methacrylate-ethyl acrylate (or butyl acrylate) copolymers.

Normally the particle size of the latex will range from about 100 to 600 nm and the latex emulsion will contain 40-50% solids.

Other Components and Processing

In the practice of the invention, a paint is prepared by dispersing hydrophobic dispersant, standard formulation surfactant, standard freeze-thaw stabilizer, standard coalescing aid, standard anti-foaming agent, and standard anti-fungus agent in water in a suitable disperser such as a Cowles disc mill, adding the dry pigment at low speed, and grinding the mixture in the disperser at a speed and for a time ,e.g., 3900 rpm for 10 minutes, sufficient to obtain the desired fineness; and then adding standard latex, water, and a concentrated solution of the associate thickener in amounts necessary to achieve the desired viscosity over the desired shear rate range.

A typical paint formulation in accordance with this invention contains 33% non-volatiles by volume, .79 v/v fraction latex, 0.21 v/v fraction pigment, 1.33 g. formulation surfactant/ 100 grams pigment and 0.75 gram hydrophobic dispersant /100 grams of pigment.

Test Methods

To determine gloss a paint is drawn down to a thickness of 0.006 inch and is immediately dried under appropriate conditions. The gloss of the dried paint film at 60 degrees and 20 degrees is measured using a Model CG-9095 Gardner MultiAngle Glossmeter. Readings are recorded 24 hours after application.

In the examples below, viscosity is reported in Krebs units (KU). The viscosity is measured in a Stormer Viscometer using a fixed shear rate at 77 degrees F. and using a variable weight to power a stirrer paddle at a predetermined rotational velocity in the paint. The weight needed for this purpose, in grams, is converted to Krebs units in the standard manner.

The following Examples illustrate this invention.

Example 1, 1A, 2 and 2A demonstrate that the combination of hydrophobic dispersant and hydrophobe modified water soluble associate thickener (EX 1 and 1A), produce better gloss and more efficient thickening per unit weight percent of the associated thickener than the combination of hydrophilic dispersant and associative thickener (2 and 2A).

EXAMPLE 1

	wt.%
TiO_2 (R-900)	21.36
Hydrophobic dispersant (TAMOL 731, diisobutylene/maleic acid copolymer)	.53
Formulation surfactant (TERGITOL 15-S-9, b-C13H27(OCH2CH2)9OH	.28
Freeze-thaw stabilizer (ethylene glycol)	1.52
Coalescing aid (TEXANOL, 2,2,4-trimethyl-1,3 pentanediol monoisobutyrate	1.52
Anti-foaming agent (COLLOID 581B)	.36
Anti-fungus agent (phenyl mercuric acetate)	.05
Latex, acrylic resin (AC-234) (based on 46% solids latex)	46.18
Water and thickener (HEUR 200, wt% based on water phase = 2.23%)	28.20

EXAMPLE 1A

A composition is formulated as in Example 1 except 1-decene/maleic acid polymer [AO(C10)/MA is used instead of TAMOL 731.

EXAMPLE 2

A composition is formulated as in Example 1 except that a hydrophilic dispersant, TAMOL 850 (poly(methacrylic acid) PMMA homopolymer), replaces the hydrophobic dispersant.

EXAMPLE 2A

A composition is formulated as in Example 1 except a hydrophilic dispersant, PMMA of approximately 5,000 molecular weight is used instead of TAMOL 731.

Latex paints prepared in accordance with Examples 1, 1A, 2, and 2A are compared in Table I.

TABLE I

	1	1A	2	2A
Stormer viscosity (KU)	104	105	109	105
Thickener wt % based on water phase	2.23	2.23	2.44	2.44
60 degree gloss	66	64	49	60
20 degree gloss	21	23	14	17

EXAMPLES 3-6

These Examples use various associate thickeners and dispersants as listed in the following:

Example	Thickener	Dispersant
3	(NP50C6)3N	AO(C10)/MA
4	"	AO(C14)/MA
5	"	AO(C18)/MA
6	"	PMMA
7	(NP100)2TMXDI	AO(C10)/MA
8	"	AO(C14)/MA
9	"	AO(C18)/MA
10	"	PMMA

For Examples 3 to 10, components such as the coalescing aid, freeze-thaw stabilizer, and the anti-foaming agent, are omitted to simplify the formulation. Gloss results for these examples are provided in TABLE II. For each thickener the combinations with hydrophobic dispersants generally provides better gloss than the combination with the PMMA hydrophilic dispersant.

TABLE II

Example	G.Thickener/ 100 grams water	Gloss 60 Degrees	20 Degrees
3	0.8	77	30
	1.2	65	30
4	0.8	74	36
	1.2	73	33
5	0.8	63	29
	1.2	64	19
6	0.8	67	27
	1.2	67	25
7	1.0	75	44
	1.7	73	39
8	1.0	74	43

		1.7	73	38
	9	1.0	74	43
		1.7	75	43
	10	1.0	59	20
		1.7	62	22

EXAMPLES 11-27

These Examples illustrate the thickening efficiency, and hence cost effectiveness, of combinations of hydrophobically modified dispersants and hydrophobe modified associate thickeners.

Four non-hydrophobe modified thickeners, viz., three poly(oxyethylene) polymers of molecular weights 100,000 (POE-100K), 35,000 (POE-35K), 12,000 (POE-12K) and hydroxyethyl cellulose (HEC), and four hydrophobe modified ethoxylate urethane (HEUR) thickeners, were used.

Table III shows the amounts of non-hydrophobe modified thickeners (nos. 12-15), and of hydrophobe modified thickeners (nos 16-19), necessary to attain 90 KU viscosity with the hydrophilic PMMA dispersant, and the corresponding amounts to attain the viscosities shown with the hydrophobic DIBMA dispersant. Only half the level of HEUR thickener is necessary to attain 100 KU dispersions with the hydrophobic DIBMA stabilized pigment versus that necessary to attain 90 KU dispersions with the hydrophilic PMMA stabilized pigment (nos 16-19). This effect is not seen with the non-hydrophobe thickeners (nos. 12-15).

Table IIIA shows results using TiO_2 pigment which has a coating primarily of alumina.

Table IIIB shows corresponding results with TiO_2 pigment which has more silica in the surface treatment. This TiO_2 pigment also needs less HEUR thickener to viscosify the dispersant stabilized with the hydrophobic DIBMA dispersant (nos. 24(b)-27(b)) than with the hydrophilic PMMA dispersant.

TABLE III

Rheology of pigment/dispersant/thickener dispersions

III A. R-900 TiO_2 pigment

No.	Dispersant	Thickener	Wt%	Viscosity (Ku)
12(a)	PMMA	POE-100K	6.1	90
12(b)	DIBMA	POE-100K	6.4	86
13(a)	PMMA	POE-35K	8.9	90
13(b)	DIBMA	POE-35K	9.2	72

14(a)	PMMA	POE-12K	11.0	90
14(b)	DIBMA	POE-12K	11.0	72
15(a)	PMMA	HEC	0.7	90
15(b)	DIBMA	HEC	0.7	91
16(a)	PMMA	HEUR-270	2.0	90
16(b)	DIBMA	HEUR-270	0.7	101
17(a)	PMMA	HEUR-200	4.2	90
17(b)	DIBMA	HEUR-200	1.8	101
18(a)	PMMA	HEUR-100	1.7	90
18(b)	DIBMA	HEUR-100	0.8	101
19(a)	PMMA	HEUR-708	1.8	90
19(b)	DIBMA	HEUR-708	0.7	101

III B. R-902 TiO_2 pigment

No.	Dispersant	Thickener	Wt%	Viscosity (Ku)
20(a)	PMMA	POE-100K	6.1	90
20(b)	DIBMA	POE-100K	6.4	86
21(a)	PMMA	POE-35K	8.9	90
21(b)	DIBMA	POE-35K	9.2	72
22(a)	PMMA	POE-12K	11.0	90
22(b)	DIBMA	POE-12K	11.0	63
23(a)	PMMA	HEC	0.6	90
23(b)	DIBMA	HEC	0.7	87
24(a)	PMMA	HEUR-270	1.9	90
24(b)	DIBMA	HEUR-270	0.7	82
25(a)	PMMA	HEUR-200	4.0	90
25(b)	DIBMA	HEUR-200	1.8	90
26(a)	PMMA	HEUR-100	1.7	90
26(b)	DIBMA	HEUR-100	0.9	100
27(a)	PMMA	HEUR-707	1.8	90
27(b)	DIBMA	HEUR-708	0.8	82

Since numerous changes may be made in the above-described examples without departing from the spirit and the scope of the disclosure, it is intended that the description be received as illustrative, and not in a limiting sense.

CLAIMS

What is claimed is:

1. A pigment particle having absorbed on its surface an hydrophobically modified dispersant interacting with an hydrophobe- modified water-soluble polymer associate thickener.

2. The pigment particle of claim 1 wherein the pigment is TiO_2.

3. A latex paint composition comprising latex, water and pigment particles, wherein the pigment particles have absorbed on their surface an hydrophobically modified dispersant interacting with an hydrophobe-modified water-soluble polymer associate thickener.

4. The pigment particle of claim 3 wherein the pigment is TiO_2.

5. The composition of claim 4 wherein the dispersant is a hydrophobic acid copolymer.

6. The composition of claim 5 wherein the dispersant is an alpha olefin/maleic acid copolymer.

7. The composition of claim 6 wherein the olefin has 5- 25 carbon atoms.

8. The composition of claim 5 wherein the dispersant is a diisobutylene/maleic copolymer.

9. The composition of claim 7 wherein the olefin is 1- decene, 1-tetradecene or 1-octadecene.

10. The composition of claim 4 wherein the associative thickener is a hydrophobe-modified ethoxylated urethane.

11. The composition of claim 4 wherein the associate thickener is a polymer formed by reacting a diisocyanate with a hydrophobe-containing poly(ethyleneoxide)$_x$ wherein x is 1-250.

12. The composition of claim 4 wherein the associate thickener is a polymer formed by reacting poly(oxyethylene)$_y$, wherein y is 50 to 750, sequentially with a diisocyanate and then with a C4-C18 alcohol or C7-C18 alkylphenol.

13. The formulation of claim 11 wherein the associative thickener is a hydrophobically modified water soluble polymer made by reacting isocyanate biuret of diisocyanate with a nonyl phenol surfactant containing from 50-100 ethylene oxide units.

14. The formulation of claim 11 wherein the associative

thickener is a hydrophobically modified water soluble polymer made by reacting tetramethylxylene diisocyanate with a nonyl phenol surfactant containing 100 ethylene oxide units.

15. The formulation of claim 11 wherein the associative thickener is a hydrophobically modified water soluble polymer made by reacting polyethylene glycol of about 595 repeating units with isophorone diisocyanate and then reacting octyl phenol with the isocyanate groups on the isophorone diisocyanate.

16. A film formed by applying the composition of claim 3 to a surface and allowing the composition to dry.

17. A latex paint composition comprising:

(a) TiO2, at least 10 volume percent;

(b) hydrophobic acid copolymer dispersant, 0.3 to 1.5 grams per 100 grams of TiO_2;

(c) associate thickener comprising:

(I) hydrophobically modified ethoxylated urethane.

(II) polymers formed by reacting a diisocyanate with a hydrophobe-containing poly(ethyleneoxide)$_x$ wherein x is 1- 250;

(III) polymers formed by reacting poly(oxyethylene)y wherein y is 50 to 750, sequentially with a diisocyanate and subsequently with a C4-C18 alcohol or C7-C18 alkylphenol;

(d) latex of acrylate or vinyl acetate copolymer;

(e) water; and

(f) optionally, formulation surfactant, freeze-thaw stabilizer, coalescing aid, anti-foaming agent, or anti-fungus agent.

18. The method of producing paint compositions of claim 4, comprising:

(a) dispersing hydrophobic dispersant, optional formulation surfactant ,optional freeze-thaw stabilizer, optional coalescing aid, optional anti-forming agent, and optional anti-fungus agent, in water, in a suitable disperser;

(b) adding TiO_2 at a low speed;

(c) grinding the mixture in the disperser at a speed and time to obtain to desired fineness; and

(d) adding latex, water and a concentrated solution of associate thickener in amounts necessary to achieve a desired viscosity.

19. A TiO_2 pigmented latex paint composition in which a hydrophobically modified dispersant is physically absorbed onto the TiO_2 and is interacting with hydrophobic groups attached to a hydrophobe-modified associate

thickener; said formulation resulting in improved gloss properties and thickening efficiency per unit weight percent associate thickener.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/09215

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C09C3/10; C09C1/36; C09D7/12; C09D7/00
C09C3/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C09C ; C09D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 134 (C-581)4 April 1989 & JP,A,63 301 262 (PENTEL K. K.) 8 December 1988 see abstract	1
A	CA,A,935 255 (CANADIAN TITANIUM PIGMENTS) 16 October 1973	
A	US,A,4 170 485 (D. W. BLAKE ET AL.) 9 October 1979 see column 1, line 63 - column 2, line 4; example 1	1,4,8

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° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
08 MARCH 1993	23. 03. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	VAN BELLINGEN I.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category°	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	PROGRESS IN ORGANIC COATINGS vol. 17, 1989, pages 155 - 173 J. S. BERGH ET AL. 'RHEOLOGY OF ASSOCIATIVE THICKENER PIGMENT AND PIGMENTED COMMERCIAL LATEX DISPERSIONS' cited in the application	
A	DATABASE WPIL Section Ch, Week 7, Derwent Publications Ltd., London, GB; Class A25, AN 89-049221 & JP,A,1 004 228 (IPPOSHA YUSHI KOGYO) 9 January 1989 see abstract	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9209215
SA 66565

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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